



## Simultaneous pH self-neutralization and bioelectricity generation in a dual bioelectrode microbial fuel cell under periodic reversion of polarity

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### HIGHLIGHTS

- Whole-cell study of polarity reversion in dual-bioelectrode MFC was first reported.
- Polarity reversion enables electricity production and buffer minimization in MFC.
- Polarity reversion improved anodic and cathodic performance.
- Useful indications were obtained for further optimization of the system.

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### ABSTRACT

In order to overcome pH membrane gradient and minimize dosage of buffer, a dual bioelectrode microbial fuel cell (MFC) with periodic reversion of polarity is conducted. The performances of the MFC before and after polarity reversion are compared to the MFC without polarity reversion and the mechanisms of the polarity reversion are investigated using electrochemical impedance spectroscopy and cyclic voltammetry. The MFC has been run continuously and stably for more than four months under periodic reversion of polarity with extreme low phosphate buffer of 5 mM. The accumulated proton in the anode and hydroxyl in the cathode are neutralized after polarity reversion but the acidification of the anode more serious than the alkalization of the cathode. Polarity reversion improve the anodic and cathodic performance due to in situ use of the accumulated proton and hydroxyl in the same electrode chamber which result in 58.3% and 36.0% increases in power density as compared to that produced before polarity reversion and by the MFC without polarity reversion, respectively. Cathode performance can be adversely affected by residual soluble organic carbons during polarity reversion due to oxygen consumption by heterotrophic bacteria in the presence of residual soluble organic carbons.

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### 1. Introduction

Microbial fuel cell (MFC) is representing an innovative and promising technology for wastewater treatment, since it can convert the energy stored in waste organic compounds to electrical energy while accomplishing wastewater treatment through a series of electrochemical reactions catalyzed by microorganisms [1–3].

One inherent technical obstacle which is so-called membrane pH gradient must be overcome because it puts an electrochemical/thermodynamic constraint on MFC performance [4–6]. In two-chambered MFC, membranes are designed to separate the anode and cathode liquids. Continuous operation of MFC results in acidification of anode caused by competitive membrane transport of nonspecific cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$ ) which are present at typically much higher concentrations than protons and accumulation of protons, whereas the cathode will become alkalized due to continuous consumption of protons for the oxygen reduction and accumulation of hydroxyl [7]. The acidification of anode suppresses bacterial respiration and thus current generation while the alkalization of cathode can lead to mass transfer limited

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proton transport to the cathodic catalyst [7,8]. Thus, high concentrations of buffer are generally needed to offset these pH changes and to ensure successful operation of the MFC. However, addition of buffer regularly is obviously not sustainable due to the high cost, especially for application in large scale wastewater treatment. In addition, the buffer of phosphates of high concentrations of usually 50–300 mM could contribute to eutrophication of the water body [8,9].

Recently, it was shown that anodophilic biofilm can catalyze cathodic oxygen reduction whereas the cathodophilic biofilm can catalyze anodic substrate oxidation [10,11]. Hereby, it could be imagined that the membrane pH gradient problem could be solved through reversion of polarity of the bioelectrode because pH can be self-neutralized when the polarity is reversed. It should be noted that these studies were conducted in a potentiostat controlled half cell or an MFC with well controlled chemical counter electrode. The MFC with dual bioelectrode run under repeated reversion of polarity would be another case because biocatalytic activity is introduced into both the anode and cathode.

In this study, we developed a dual bioelectrode two-chamber MFC which could run under periodic reversion of polarity to minimize buffer dosage with a long-term stability. The performances of the MFC before and after polarity reversion were compared to the MFC without polarity reversion in terms of power output and electrode polarization and the mechanisms involved in the polarity reversion were investigated using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Our study could provide a scientific basis for construction of a novel MFC to overcome pH membrane gradient and minimize buffer dosage.

## 2. Materials and methods

### 2.1. Construction of dual bioelectrode two-chamber MFC

A two-chamber MFC with the electrodes separated by a cation exchange membrane (CEM) (Zhejiang Qianqiu Group Co., Ltd. China) (4 × 4 cm in diameter) was designed. The CEM was pre-treated by boiling in  $H_2O_2$  (30%) and deionized water, followed by 0.5 M  $H_2SO_4$  and deionized water, each for 1 h, and then stored in deionized water. The net working volume of each chamber was 256 mL (8 cm × 8 cm × 4 cm). Carbon felts with a projected surface area of 30  $cm^2$  (5 cm × 6 cm) were used as the anode and cathode. Prior to use, carbon felt were cleaned by soaking in acetone overnight and then washed thoroughly with deionized water. The anode and cathode were placed at approximately 1 cm from the CEM, respectively. Titanium wires were used to connect the circuit with an external resistance of 500 ohms. All exposed metal surfaces were sealed with a nonconductive epoxy.

### 2.2. Start-up and running of dual bioelectrodes two-chamber MFC

#### 2.2.1. Pre-acclimation of electrically active biofilm

The two bioelectrodes with a mature electrically active biofilm were initially obtained from two air-cathode single-chamber MFC fed with glucose. The MFCs were inoculated with a mixture of aerobic sludge and anaerobic sludge (1:1, v:v) from.

Liede municipal wastewater treatment plant of Guangzhou city, China. Before inoculation, the sludge were washed three times using deionized water to remove soluble carbon sources and were then filtered through a 0.22-mm pore size sieve to remove impurities. The sludge was added to the MFCs at a final concentration of 2 g volatile suspended solids per reactor volume. Glucose (500 mg COD/L) was fed in 50 mM phosphate buffer solution (PBS, pH 7.0) containing (per liter deionized water): KCl, 0.13 g;  $NaH_2PO_4 \cdot 2H_2O$ ,

3.32 g;  $Na_2HPO_4 \cdot 12H_2O$ , 10.32 g;  $NH_4Cl$ , 0.31 g, and trace metal (12.5 mL  $L^{-1}$ ) and vitamin (12.5 mL  $L^{-1}$ ) solutions [12]. The MFCs run under anaerobic fed-batch conditions at 500 ohms for more than three months until the mature electrically active biofilms were grown on the surface of the anode.

#### 2.2.2. Fabrication and running of dual bioelectrodes two-chamber MFC

Once the mature electrically active biofilms was obtained, the bioanodes were taken out of the two air-cathode single-chamber MFC and were incorporated into a two-chamber MFC as previously stated. The anode of the MFC was fed with a medium which used in the air-cathode single-chamber MFC previously. The same medium was used in the cathode except for the replacement of glucose by  $NaHCO_3$  (0.4 g  $L^{-1}$ ). The MFC run at batch-fed mode and under periodic reversion of polarity according to following procedure:

Start-up: the anode was fed glucose (500 mg COD/L) contained the medium previously used in air-cathode single chambered MFC. Although the pH buffering in the MFC was dependent on the neutralization of pH through polarity reversion, 5 mM PBS was used for ensuring successful start up the MFC and preventing fast acidification of anolyte. The anodic chamber was sealed off to maintain anaerobic condition. The cathodic chamber was continuously aerated with ambient air at a flow rate of 3  $L h^{-1}$ . The MFC was stopped running when the voltage decreased below 30 mV.

Polarity inversion: the polarity of the MFC was reversed without refreshing the anodic and cathodic liquid. The anode (corresponding to the cathode in previous operation) was supplemented with glucose and was sealed off to maintain anaerobic condition, while the cathode (corresponding to the anode in previous operation) was supplemented with  $NaHCO_3$  (0.4 g  $L^{-1}$ ) and continuously aerated with ambient air at a flow rate of 3  $L h^{-1}$ . During this process, the accumulated acidity or alkalinity in the electrolyte was neutralized.

To minimize mass-transfer limitations, both the anode and cathode were slowly mixed using a small magnetic stirrer. No active pH control of the electrolyte was conducted during the entire running of the MFC. All experiments were carried out at least in duplicate, in a constant-temperature room ( $30 \pm 1 ^\circ C$ ), and the average value was reported for all data. The schematic operation of the MFC was shown in Fig. 1.

#### 2.3. Analytics and calculations

##### 2.3.1. Electrochemical analyses

The voltage difference between anode and cathode (V) was recorded every 11 min using a precise multimeter and a data acquisition system (Model 2700, Keithly Instruments, USA).

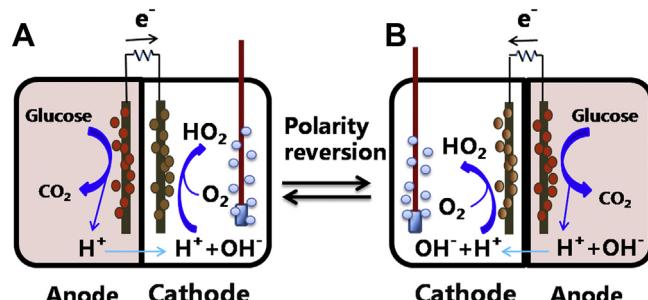


Fig. 1. Schematic (A) and picture (B) of the dual-bioelectrode MFC operated under periodically inversion of polarity.

Polarization curves were obtained by applying a different external resistance (from 5000  $\Omega$  to 50  $\Omega$ ) to the circuit and the maximum sustainable voltage was recorded for each resistance. Then, the gained voltage and current values were converted to Power density ( $P$ ,  $\text{mW m}^{-2}$ ) according to  $P = U^2/RA$ , where  $U$  (V) is the cell voltage,  $R$  ( $\Omega$ ) is the resistance, and  $A$  ( $\text{m}^2$ ) is the projected area of the anode [13].

The potentials of the anode and cathode were also measured across various resistances (5000–50  $\Omega$ ) and against saturated calomel electrode (SCE, +0.242 V vs. normal hydrogen electrode, NHE).

CV and EIS were adopted to characterize the electrochemical activity of biofilm on electrode surface and delineate resistances in electrode, respectively using an electrochemical workstation (Model 2273, Princeton Applied Research). All the electrochemical assays were performed *in situ* in a conventional three-electrode cell mode by considering anode and cathode as working and counter electrodes and vice versa, against SCE reference electrode. Prior to each measurement, the MFC run under open circuit condition for more than 1 h until open circuit potential was stable. CV was conducted by applying a potential ramp to the working electrode (anode/cathode), at a scan rate of 20  $\text{mV s}^{-1}$  (minimum of 5 scans) over the range from −0.6 V to +0.12 V. EIS measurements were carried out in a frequency range of 100 kHz to 1 mHz with an ac signal of 10 mV amplitude. The obtained data were fitted according to predetermined equivalent electrical circuit.

### 2.3.2. Monitoring of pH

The pH were continuously monitored by an on-line pH meter (Mettler-Toledo, Switzerland) connected to a personal computer.

## 3. Results and discussion

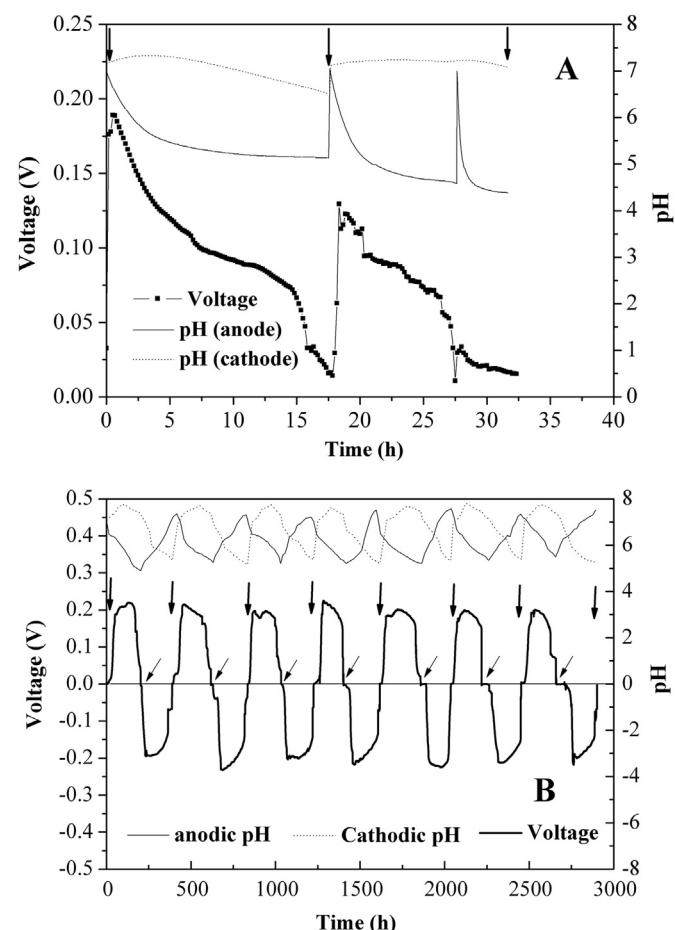
### 3.1. Buildup of pH gradient impedes electricity production in the absence buffer

A dual bioelectrode MFC with well-acclimated biofilm anode and cathode was used to test the electricity production in the absence of buffer. As shown in Fig. 1, continuous batch run of the MFC in the absence of buffer resulted in fast acidification of anolyte which even resulted in decreases in catholyte pH over time due to proton transport through the membrane from anodic chamber to cathodic chamber. As a consequence, electricity generation was hampered due to suppression of electrochemical activity of the anodophilic biofilm. The anodic pH quickly decreased from 7.0 to 5.0 accompanied by fast decrease in voltage from 0.19 V to background levels within 18 h after addition of 500 mg COD/L of glucose-contained and buffer-free medium. Subsequent batches, i.e., addition of fresh glucose-contained and buffer-free medium demonstrated faster acidification of anolyte and drop in voltage than the first batch. At the third batch, glucose addition no longer resulted in a clear voltage response as the anodic pH decreased from 7.0 to 4.5 within 5 h. Although replacement of the anolyte alleviated the acidification in bulk solution, but the acidity could accumulate to a high level inside the biofilm because the acidification of the anodic biofilm was not intrinsically solved [8]. This result revealed that the fast decreases in voltage were mainly attributed to the fast acidification of the anodic biofilm.

### 3.2. Polarity reversion enables long-term stable voltage output with extremely low buffer

In order to prevent fast acidification of anolyte and prolong cycle period, the MFC was supplemented with extremely low concentration of PBS (5 mM) and was run under periodic reversion of

polarity. Fig. 2 shows long-term voltage outputs and pH variation in anolyte and catholyte of the dual bioelectrode MFC run under periodic reversion of polarity. Prior to polarity reversion, the anodic pH decreased from around 7.0 of the start-time to nearly 5 of the end-time caused by microbial oxidation of glucose and proton production and accumulation of proton due to the resistance of the CEM, while the cathodic pH firstly increased from around 7.0 to 7.6–7.8 then decreased gradually and decline to 7.3–7.5 at the end-time, due to the fact that the proton in the anode was at low concentration in the initial stage, probably because of the low reaction rate of anodic microbial oxidation of glucose, and the protons transport through the CEM were limited to support the cathode reaction using oxygen as oxidant and cathodic pH increased. However, as the anodic reaction progress and accelerated depletion of substrate, proton accumulated to high concentration in the anolyte and diffused to cathode through the CEM, with the result that the cathodic pH was declined and neutralized. After polarity reversion, the proton in the cathode (corresponding to previous anode) was rapidly consumed and the cathodic pH was recovered to 7.0–7.5, while the anode (corresponding to previous cathode) pH further decreased to 5.2–5.4 due to accumulation of proton. Thus, the self-neutralization was completed. It should be noted that the cathodic pH underwent further decrease after polarity reversion, however, the electricity generation was not hampered, indicating that the biofilm bacteria has high tolerability to acid environment.



**Fig. 2.** Voltage output and pH vs. time in the buffer-free MFC (A) and the MFC operated under periodically inversion of polarity with addition of 5 mM PBS (B). Anodic voltage is positive and cathodic voltage is negative. Thin arrows indicate polarity reversion while bold arrows indicate replacement of anodic and cathodic medium.

The relative low cathodic pH also indicated that there is considerable room for performance improvement of the cathode with respect to the biocatalyzed oxygen reduction process.

Compared to the unexpected decrease in cathodic pH before polarity reversion due to cross-membrane transport of protons, the cathodic pH underwent continuous increase after polarity reversion, indicating that the cathode performance was significantly improved after polarity reversion because the accumulated protons were fast consumed by the accelerated biocatalytic oxygen reduction.

During pH self-neutralization, the polarity reversion also resulted in stable voltage outputs and there was no noticeable difference in voltage outputs before and after polarity reversion (0.2–0.23 V). Hence, the bioelectrode alternate catalysis of anodic electron transfer and cathodic oxygen reduction was demonstrated.

The dual bioelectrode MFC run steadily over 120 days under repeated reversion of polarity in which stable voltages output and sustainable pH self-neutralization were observed. This result indicates that it is feasible for simultaneous pH self-neutralization and bioelectricity generation in dual bioelectrode MFC through periodic reversion of polarity.

### 3.3. Power output and polarization before and after polarity reversion

By varying the external resistance, we obtained the power density and polarization curves, which evaluated the performance of electricity generation of the dual bioelectrode MFC run under periodic reversion of polarity. Fig. 3A showed that polarity

reversion improved performance of the MFC, as evidenced from the increased power output. The maximum power density achieved after polarity reversion was  $38 \text{ W m}^{-2}$  at the current density of  $0.15 \text{ A m}^{-2}$ , which was 58.3% and 36% higher than that produced before polarity reversion ( $24 \text{ W m}^{-2}$ ) and by the MFC without polarity reversion ( $28 \text{ W m}^{-2}$ ), respectively. The internal resistance which is inversely proportional to the power density was determined through the slope of line of polarization curves (Logan et al., 2006). The internal resistance of the MFC before polarity reversion was  $1100 \Omega$ . The internal resistance decreased to  $495 \Omega$  (by 55%) after polarity reversion which was also 48% lower than that for the MFC without polarity reversion ( $956 \Omega$ ).

To further examine the effects of polarity reversion on electricity generation, the electrode potentials were measured as a function of current by varying the external resistor (Fig. 3B). The electrode potentials curve showed that polarity reversion improved the anode and cathode performance simultaneously. The slope of both the anodic and cathodic polarization curve after polarity reversion showed more gentle decreases as compared to that of before polarity reversion with increasing current density, evidently indicating alleviative polarization in the anode and cathode after polarity reversion. It appears that the increases in power output after polarity reversion was attributed to the improvement in the anode and the cathode performance. The possible reason for the improvement was that the accumulated protons at the anode and hydroxyl at the cathode were used as their respective reactants after polarity reversion, which kinetically promoted the half cell reaction rates of the MFC [10,11].

The MFC run under periodic reversion of polarity were also compared with the MFC without polarity reversion. Since both MFCs are configured in the same way except for the run mode, we can see that, before polarity reversion, both the MFCs exhibit small difference in their anode potentials while the slope of the cathodic polarization curve of the MFC run under periodically inversion of polarity showed a more rapid decrease than that of the MFC without polarity reversion, indicating severe polarization of the cathode. However, the cathodic polarization was alleviated after polarity reversion which indicated by a similar polarization curve slope to that of the MFC without polarity reversion. Meanwhile, evidence from the anodic polarization curves showed that polarity reversion also led to better anode performance than that of the MFC without polarity reversion.

Lower cathode potential before polarity reversion as compared to that of the MFC without polarity reversion could be attributed to oxygen consumption by bacteria in presence of residual soluble organic carbons in the bulk solution and inside biofilm which could compete for oxygen with the cathode and result in decreases in cathodic potential [14]. The cathode polarization after polarity reversion was similar to that of the MFC without polarity reversion, probably due to that the positive effect of polarity reversion on enhancement of half-reaction of the cathode exceeded the negative effect of residual organic carbons on oxygen consumption, since both effects have opposite contributions to cathode performance.

### 3.4. Electrochemical characterization of bioelectrode before and after polarity reversion

To investigate the effect of polarity reversion on impedance variation in electrodes, the electrode impedance before and after polarity reversion were tested using EIS technology. Nyquist plots deduced from impedance data are given in Fig. 4. As clearly indicated by the results of the Nyquist plots, charge-transfer resistance ( $R_{ct}$ ) which is reflected by the diameter of the semicircular arc of the curve overwhelmed the anode impedance and the solution resistances ( $R_s$ ) appear to be insignificant (Fig. 4A). Smaller  $R_{ct}$

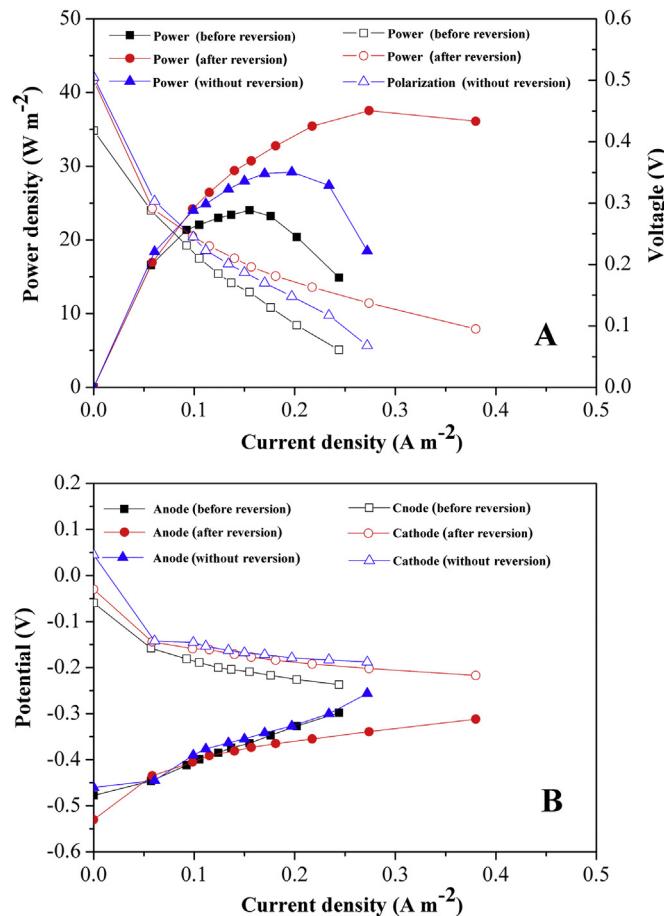


Fig. 3. Power density and polarization (A) and electrode potentials (B) curves of the MFC before and after polarity reversion and the MFC never polarity reversion.

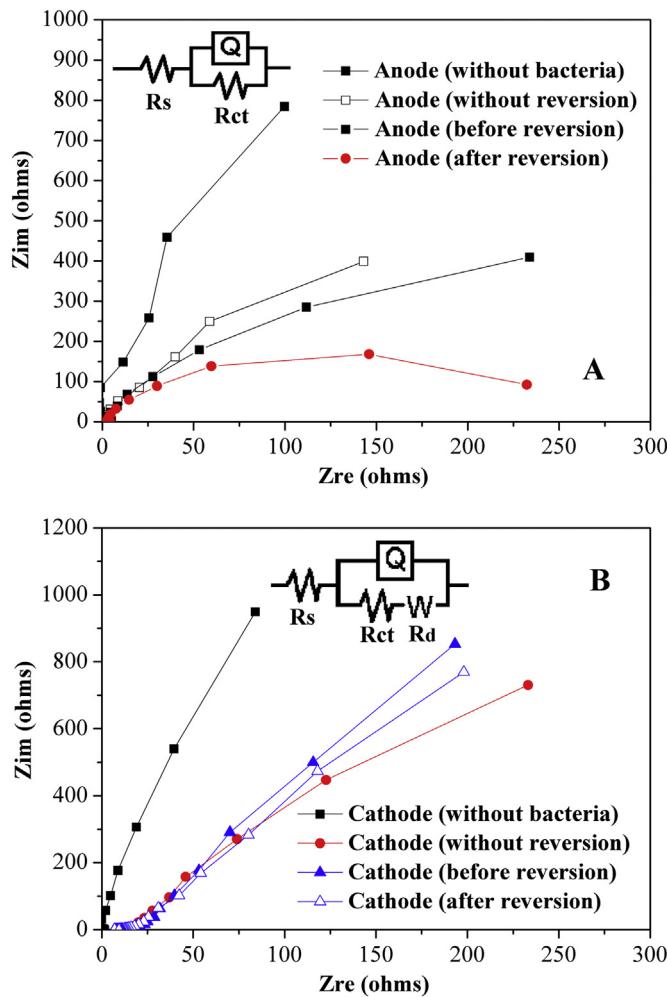


Fig. 4. Nyquist impedance spectra of anode (A) and cathode (B) of the microbial fuel cell before and after polarity reversion.

indicates a faster electron-transfer rate between electrode and electrolyte [15]. The anode  $R_{ct}$  before polarity reversion was  $1171\ \Omega$  while the anode  $R_{ct}$  sharply decreased to  $337\ \Omega$  after polarity reversion, indicating that polarity reversion significantly reduced the electron transfer resistance and revealed a faster electron transfer rates between the electrode and electrolyte. One possibility is that the solution contained some redox active compounds excreted by microorganism before polarity reversion, which can accelerate electrons transfer from bacteria to the anode [16]. The anodic  $R_{ct}$  before and after polarity reversion were all lower than that of the MFC without polarity reversion ( $1327\ \Omega$ ), demonstrating improved the anode performance through polarity reversion.

Fig. 4B shows the typical Nyquist plots of cathodes before and after polarity reversion, never polarity reversion and without biofilm. Each of the plots is a straight line, indicating that the impedance of the cathode was dominated by the cathodic charge transfer resistance for the cathode/electrolyte interface ( $R_d$ ). The  $R_d$  significantly contributed to the oxygen reduction process. The cathode with polarity reversion had higher  $R_d$  than the cathode without polarity reversion, might due to the shortage or limited diffusivity of oxygen in bulk solution and inside biofilm [17] which could be a consequence of oxygen consumption by bacteria in presence of residual soluble organic carbons [14].

The electrode without biofilm resulted in extremely high anodic  $R_{ct}$  and cathodic  $R_d$  as compared to that of the biofilm

electrode. Thus the present microorganisms were a prerequisite for run of the dual bioelectrode MFC and thus responsible for both biocatalyzed anodic and cathodic electron transfer.

CVs were performed to reveal the biocatalytic activities of the electrode biofilms before and after polarity reversion in a dual bioelectrode MFC (Fig. 5). Based on the CVs of anode, there were no significant changes in the relative position of the redox peaks before and after polarity reversion, indicating that the polarity reversion has less effect on the electrochemical properties of the anode (Fig. 5A). However, the anode after polarity reversion resulted in larger current responses than the anode before polarity reversion in potentials ranging between  $-0.6\text{ V}$  and  $0.15\text{ V}$  which is consistent with the result of the EIS and polarization of the anode, indicating that the performance of the anode was indeed improved after polarity reversion.

In contrast, the anode without polarity reversion exhibited a different voltammetric behavior as compared with the anode with polarity reversion, implying that the polarity reversion resulted in change in biofilm characteristics. From this result it may be concluded that the composition of the microbial biofilm with respect to the dominating, electroactive, species, was measurably affected by long-term polarity reversion. In further studies it will have to analyze the bacterial diversity in biofilms with and without polarity reversion to confirm the conclusion.

The catalytic behaviors of oxygen reduction by the biocathode with and without polarity reversion were shown in Fig. 5B. It can be

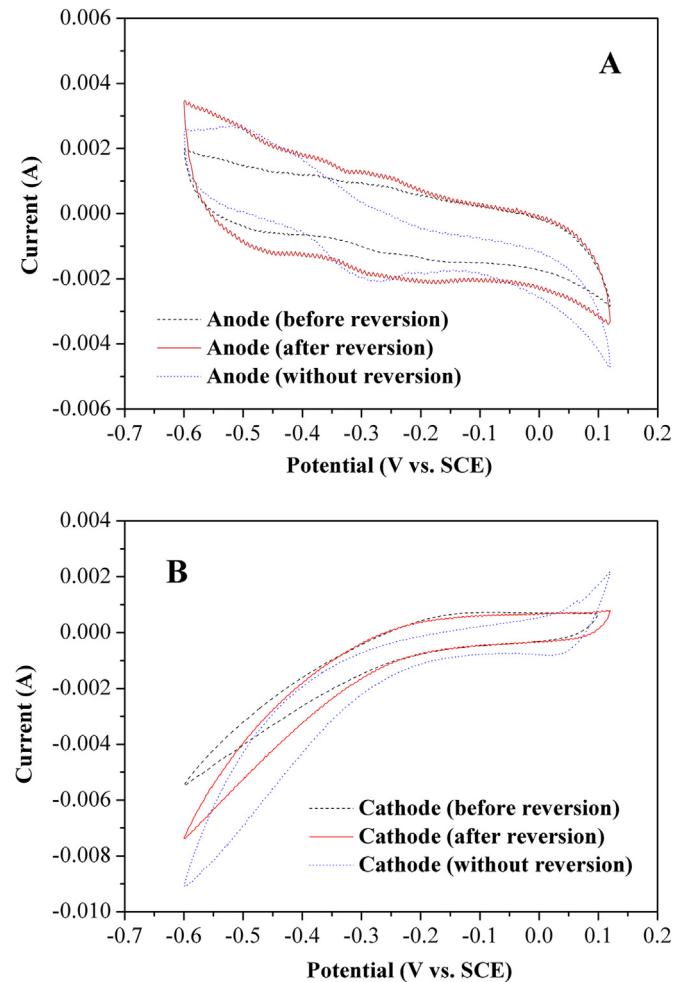


Fig. 5. Cyclic voltammograms of the anode (A) and cathode (B) of the microbial fuel cell before and after polarity reversion.

seen that the biocathode after polarity reversion showed exactly the same catalytic behavior, but of lower maximum current compared to the biocathode before polarity reversion, implying the improvement in oxygen reduction process of the biocathode after polarity reversion. This result could be expected because the accumulated protons before polarity reversion could kinetically promoted the biocatalyzed oxygen reduction reaction in the cathode after polarity reversion.

The biocathode without polarity reversion performed similar catalytic behavior as compared with the biocathode with polarity reversion but showed lower maximum current, indicating better catalytic activity toward oxygen reduction. This result was consistent with previous speculation on EIS that aerobic oxygen consumption by the bacteria in presence of residual soluble organic carbons before polarity reversion could diminish oxygen supply for the cathode. In addition, the excessive growth of the bacteria in presence of residual soluble organic carbons would result in formation of thick biofilm on the surface of the cathode which could also decrease the cathode potential due to increased diffusion resistance of dissolved oxygen.

To confirm above speculation, the amounts of the soluble organic carbons which were expressed in COD in the biocathode with and without polarity reversion were measured and plotted against time (Fig. 6). As showed in Fig. 6, the biocathode with polarity reversion was much higher in initial COD concentration than the biocathode without polarity reversion and it was apparent that the decreases in COD with time were attributed to biodegradation which was an oxygen-consuming process under the biocathode run condition.

Small amounts of COD was also detected in the biocathode without polarity reversion indicating substrate crossover through the membrane from the anode to the cathode, however, the amounts of COD of  $4.8 \text{ mg L}^{-1}$  were much lower than that of the biocathode with polarity reversion ( $27\text{--}32 \text{ mg L}^{-1}$ ) and thus have negligible effect on the cathode performance. Substrate crossover occurs commonly in the two chambered MFC using membrane for separating anodic and cathodic chamber because of molecular diffusion and electroosmosis [18].

### 3.5. Implication of the findings

The electrocatalytic biofilm can alternately catalyze anodic substrate oxidation and cathodic oxygen reduction is not entirely

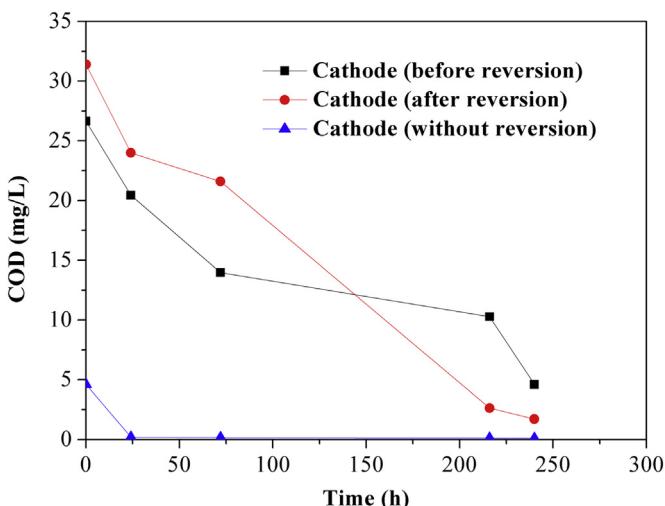


Fig. 6. Variation of COD with time in the biocathode with and without polarity reversion.

new. For example, Cheng et al. found that an anodophilic biofilm developed over many months under strictly anaerobic conditions could sustain fully oxygenated conditions without measurable side effects [10]. Strik et al. developed a solar energy powered MFC with a reversible bioelectrode in which an evolved bioelectrode with complex biofilm including algae, bacteria and protozoa were responsible for both biocatalyzed anodic and cathodic electron transfer dependent on dark and illumination [11]. However, both studies mentioned above were conducted in a potentiostat controlled half cell or an MFC with well controlled chemical counter electrode in order to minimize the effect of the counter electrode. In contrast, the performances of the MFC run under whole-cell mode were dependent upon both anode and cathode performance. Thus, whole-cell study of the performance of dual-bioelectrode MFC run under polarity reversion is challengeable because the electricity generation process could become more complex than that of half cell because biocatalytic activity is introduced into both anode and cathode. In the present study, we demonstrated for the first time that simultaneous pH self-neutralization and bioelectricity generation can be achieved using dual-bioelectrode MFC run under polarity reversion. However, some issues surrounding to the findings should be further addressed in order to improve the performance of the MFC. Firstly, the rates of anode acidification exceeded cathode alkalization which even resulted in acidification of the cathode indicated that there remains much room for performance improvement of the cathode. Furthermore, the residual soluble organic carbons could adversely affect the cathode performance due to oxygen consumption for heterotrophic bacteria growth and formation of thick biofilm which resulted in shortage and increased diffusion resistances of the dissolved oxygen in the cathode. Thus, it would be advisable to prolong running period of the MFC until the soluble organic carbons was depleted or increase the dissolved oxygen concentration through improving aeration conditions. Secondly, the effect of operation parameters such as initial carbon source concentration, solution chemistry, external resistor and membrane on the performance of the MFC should be considered because all of the parameters are directly related to the biocatalytic anodic and cathodic reaction. Furthermore, establishment of correlation between the operation parameters and biocatalytic activity of the electrocatalytic biofilm would help to give a comprehensive insight on the essence of the MFC under polarity reversion. Thirdly, effective strategies for performance optimization of the MFC described here can be obtained by addressing all of the factors affecting anodic and cathodic performance and their interactions.

### 4. Conclusions

Simultaneous pH self-neutralization and bioelectricity generation was achieved using a dual-bioelectrode MFC run under periodic reversion of polarity with 5 mM PBS. The buildup of pH membrane gradient in the MFC was solved because the accumulation of proton in the anode and hydroxyl in the cathode can be neutralized after polarity reversion. Polarity reversion improved the electricity generation performance of the MFC by 58.3% and 36% increases in power density as compared to that produced before polarity reversion and by the MFC without polarity reversion due to reduction in anodic and cathodic polarization. The accumulated protons in the anode and hydroxyls in the cathode before polarity reversion can be used in situ in the same electrode chamber after polarity reversion which kinetically promoted the half cell reaction rates of the MFC. Faster acidification of the anode than alkalization of the cathode indicated considerable room for performance improvement of the cathode. Residual soluble organic carbons could adversely affect cathode performance during polarity

reversion due to oxygen consumption by heterotrophic bacteria in the presence of soluble organic carbons.

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